Report 108-M7

INVESTIGATION OF ZEOLITE MEMBRANES FOR FUEL CELLS

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1.0 INTRODUCTION AND SUMMARY

During the current contract period experimental work has continued in the development and evaluation of inorganic membranes for hydrogen-oxygen fuel cell application. Special emphasis has been on completing the preparation of the samples called for by the statistical plan for optimizing membrane composition and preparation techniques and measuring tneir transverse strength and electrical conductivity. All twenty of these compositions have been prepared and sintered and transverse strengths have been obtained. The electrical conductivities of these materials are now being run and are about 50% complete. Additional work was also done on vacuum dried materials and it was found that vacuum drying a 1 ZrO_2:1 H_3PO_4:1 "Zeolon H" composition at 95°C increased transverse strength from 2381 psi to 5050 psi - an increase in strength of more than 100%.

Conductivities for four of the membrane compositions taken from the statistical series are reported. It was found that a linear relationship exists between resistivity and relative humidity and that the resistivities at 100% relative humidity fall between 35 and 65 ohm-cm. It was also determined that the resistivity of these membranes decreases as the ratio of H_3PO_4 to ZrO_2 and "Zeolon-H" increases.

Additional fuel cell operating data is reported comparing membranes prepared from the same composition but sintered at temperatures ranging from 250° to 750°C.

The nature of the statistical analysis being made in order to optimize preparation techniques is discussed. The results of this analysis will be covered in the final report.

Because of time required to prepare the final report covering all of the work done since the beginning of the project in June 1962, little new experimental work will be started during the current period. The work in progress will be completed whenever possible and the results will be included in the summary report.

2.0 EXPERIMENTAL WORK AND DISCUSSION

2.1 Membrane Composition Studies

All twenty of the compositions, outlined in the revised statistical plan for optimizing composition and preparation techniques in inorganic fuel cell membrane preparation, were prepared during the month. No particular difficulty was encountered in the preparation, drying, granulation, pressing or sintering of these materials.

The transverse strength of these compositions was determined. Three samples of each of the twenty compositions in the series were tested and the Modulus of Rupture values are shown in Table I. These data are now being processed for statistical evaluation and the analysis of these findings will be available in the final report.

Although direct analysis of the data thus far obtained for statistical evaluation is difficult, it can be seen that the best strength values are obtained with compositions dried at intermediate times and temperatures. Increasing drying temperature above 150°C tends to decrease strength, and generally, long drying times reduce strength. It can also be noted, that lower strength results from too high or too low a H_3PO_4/"Zeolon H" ratio. These results are consistent with previous findings and confirm results which have been reported.[1] It is apparent that the development of maximum transverse strength in phosphate bonded zirconia membrane containing "Zeolon H" or other water balancing agents depends to a large degree on the drying and sintering temperatures used in processing the materials. With a given composition, there is a definite amount of chemical reaction possible between the phosphoric acid and the other ingredients during drying and sintering, depending upon the times and temperatures used. If drying is carried out at relatively low temperatures and for short periods of time, only a small part of these chemical reactions occur during dehydration of the composition. When the dried material is subsequently granulated, pressed into membrane form and sintered, most of the chemical reactions will take place during sintering. These bonding reactions produce strength in the sintered membrane and the highest strength results from having the maximum amount of these reactions taking place during sintering. If the materials are dried at relatively high temperatures and for long periods of time, a large proportion of the bonding reactions take place during drying and do not contribute to the ultimate strength of the sintered fuel cell membrane. When the phosphoric acid content of a membrane composition is low enough to permit granulation of the material and membrane pressing without drying, all of the bonding reactions take place during sintering. As reported in 108-M6, the strength of a 2 ZrO_2:1 H_3PO_4:1 "Zeolon H" composition was doubled by eliminating the drying operation.[2]

As it is impossible however, to eliminate the drying operation except for compositions which are very low in H_3PO_4 content, the use of vacuum drying in the preparation of membrane materials was investigated. The oven which has been used for material drying was modified for vacuum drying by placing an aluminum dessicator in it. A hole was drilled in the dessicator cover and filled with a vacuum hose connection. The vacuum hose was connected through the oven vent hole to a suitable vacuum source. Samples placed in the dessicator can be dried at controlled temperatures and vacuum conditions. It was found that when a 1 ZrO_2:1 H_3PO_4:1 "Zeolon H" composition was vacuum dried for 40 hours at 90°C and 30 in. of mercury, transverse break strength increased to 5050 psi. This is more than a two-fold increase in strength as compared to the same composition prepared by oven drying for 15 hours at 160°C. It is apparent from these favorable findings that membrane strength can be substantially increased by vacuum drying which permits low temperature moisture removal. Low temperature drying minimizes the amount of reaction taking place between the H_3PO_4, ZrO_2 and "Zeolon H" during drying and, as a result, most of these reactions take place during membrane sintering where they are effective in producing membrane strength. As a result of these finding, additional vacuum drying studies are being made. It is apparent that strong membranes can be produced by appropriate selection of composition, drying and sintering conditions.

The strongest membrane produced thus far was No. 191-100 which had a Modulus of Rupture of 6025 psi and contained 2 ZrO_2:1 H_3PO_4. The second strongest membrane (No. 036-054) was 1 ZrO_2:1 H_3PO_4; 1 "Zeolon H".

In order to evaluate the effect of sintering temperature on membrane strength, various membrane compositions were prepared and sintered at 250°C, 500°C, 750°C, and 1000°C. After sintering, the transverse strength of these samples was determined and their electrical conductivity is now being measured. These materials are also being evaluated in the fuel cell in order to correlate the effect of sintering temperature with operation in the fuel cell. It was found that sintering composition 191-050 (1 ZrO_2/H_3PO_4:1 H_3PO_4:1 "Zeolon H" plus 5% ZrO_2 fibers) at 500°C produced maximum transverse strength as compared with higher and lower sintering temperatures. Sintering composition 191-050 at 250°C reduced the transverse strength from 2760 ± 90 psi to 1450 psi and sintering at 750°C and 1000°C resulted also in decreased transverse strength. These results are shown in Table II and Figure 1. The results indicate that maximum strength is obtained at about 500°C and a thorough study of the temperature range between 250°C and 750°C will now be made to determine the effects of sintering temperature for various compositions on transverse strength, conductivity and fuel cell operation. This work will be performed on compositions selected from the statistical series being studied in which the effect of other preparative conditions are being investigated.

2.2 Conductivity Measurements

The resistivities of four different membranes were determined as a function of relative humidity at each of three temperatures using the apparatus described in previous monthly reports. Resistivities reported represent the average value for three individual membranes with the error indicated as standard deviation.

The resistivities of membranes for the first four members of the 20 member statistical series are reported. Upon completion of the required measurements of conductivities for all of the members of this statistical series, the dependence of conductivity upon chemical composition, sintering temperature, and firing temperature will be deduced.

The resistivities of four different membranes formed from ZrO_2, H_3PO_4, and "Zeolon H" are presented in Tables III to VI. Membranes differ in either chemical composition or the drying conditions employed. All of these membranes were sintered at 500°C.

A comparison of the resistivities at 104°C of three different membranes each containing 30 percent by weight ZrO_2 but different H_3PO_4/"Zeolon H" ratios are illustrated in Figure 2. Examination of this figure shows:

1. A linear relationship between the logarithm of resistivity and relative humidity.

2. The intercepts of the three straight lines each representing a different membrane composition in the statistical series fall in the range from 35 to 65 ohm-cm upon extrapolation to 100 percent relative humidity.

3. The resistivity of a membrane with a fixed weight of ZrO_2 decreases as the ratio of H_3PO_4/"Zeolon H" increases, assuming that conductivity is not markedly affected by drying conditions. This tentative assumption is in conformity with the fact that membrane numbers 131-030 and 131-026 prepared under different drying conditions exhibit essentially the same resistivities as shown in Table V and VI.

2.3 Fuel Cell Operation

Fuel cell evaluations of experimental compositions were continued with principal emphasis on a series of 191-050 membranes (1 ZrO_2/H_3PO_4: 1 H_3PO_4:1 "Zeolon H") Table VII and Figure 3 compare recent fuel cell runs using this membrane with Run No. 25. Several details merit comment.

The slopes of the curves in Figure 3, with one exception, show a consistent internal cell resistance of about 0.4 ohm with this membrane. (The exception is discussed below).

Runs No. 33, 34, and 35 all showed decreased or no performance at 90°C and no performance at 95°C, in direct contrast to Runs No. 11 (Report 108-M5, Table II) and No. 25 where performance was little changed at 90° and 95°. The membranes used in Run No. 11 and 25 were pressed and sintered within a few days after preparation of the material. The membranes used in Runs No. 33, 34, and 35 were pressed and sintered after the dried and granulated material had been stored in a sealed glass jar for approximately 90 days. It is probable that a slow chemical alteration of the unsintered material is responsible for the change in behavior of the membranes prepared from the "old" material.

Run No. 33 in which the membrane was sintered at 250°C resulted in the best cell performance to date (50 ma/cm^2 at 0.5 volts). As membrane No. 191-050 sintered at 750°C produced better cell performance than when it was sintered at 500°C although internal cell resistance was reasonably uniform, it is apparent that factors other than membrane sintering temperature are involved in the performance level of membranes in the analytical fuel cell. This is further confirmed by the evaluation of the same composition sintered at 250°C. In this case the cell did not perform as well at 90°C even though the cell resistance was less than at 65°C. It is probable that there is variation in the effective catalyst area from one test to another even though the electrode area and the technique for applying the catalyst are carefully controlled. Additional fuel cell evaluations will be necessary in order to identify the other significant variables so they can be evaluated and effectively controlled.

Figure 3 illustrates an additional unexplained phenomenon; with one exception (membrane sintered at 250°, cell operated at 65°C) fuel cell assemblies exhibiting open circuit potentials above 0.9 volts, have an activation polarization; that is, the polarization curve departs from a straight line as the current density approaches zero. Assemblies with open circuit potentials below 0.9 volts do not show this polarization.

Exploratory work with the objective of improved methods of assembling the electrode, catalyst and inorganic membrane is continuing.

2.4 Statistical Design

Experimentation has been conducted on the effects of composition, drying times and temperatures on conductivity and transverse strength of fuel cell membranes. The experimental design being investigated is a central composite rotatable design for three independent variables.* In these experiments, compaction pressures, and sintering times and temperatures are being held constant at what is considered to be a near optimal level based on previous experimental results.

Early in the experimental program it was discovered that certain combinations of the three independent variables (membrane composition, drying time, and drying temperature) led to unproducible specimens. The experimental design was revised accordingly to allow the percentage of phosphoric acid to vary between 16% and 30%, drying time to vary between 20 and 60 hours, and drying temperatures to vary between 140°C and 160°C. These ranges all yield producible membranes.

The experimental design calls for 20 factor combinations. Three membranes were fabricated for each factor combination, yielding a total of 60 measurements each for the conductivity analysis and the transverse strength analysis. The transverse strength measurements have been completed and the statistical analysis is being made. The conductivity experiments will be completed in another week, providing the necessary data for the second statistical analysis. These analyses will be performed by desk calculator.

A second degree or quadratic response surface will be fitted to the experimental data if the results of the statistical analysis justify it. The fitting of the quadratic response surface will permit location and exploration of the region of optimum factor combination. In addition to locating the region of optimum response, it may be of value to explore how strength and conductivity vary in the neighborhood of the maximum response. The reason for this is that it may be easier, cheaper, or quicker to fabricate membranes which vary slightly from the optimum combination. Exploring strength and conductivity properties in the region of optimum response should reveal how much these two properties are degraded as one moves away from the optimum combination.

Additional experiments can then be designed either to extend those parts of the initial ranges of the three independent variables that appear to lead to an optimum combination of factors or to investigate more intensively a region in the first experiments that appears to contain the area of maximum response. Once this area is delineated, additional variables such as compaction pressure, and sintering time and temperature could be added to the experimental design in subsequent experiments.

*Cochran, W. G. and Cox, G. M., Experimental Designs, Second Edition, John Wiley and Sons, Inc., New York, 1962, pp. 349-353.

REFERENCES

1. "Investigation of Zeolite Membrane Electrolytes for Fuel Cells," NASA Contract NAS 7-150, Monthly Progress Report for Period Ending 7 December 1963, Astropower, Inc. Report 108-M6, p 2.

2. Ibid.

TABLE I

TRANSVERSE STRENGTH OF INORGANIC FUEL CELL MEMBRANES

Sample No.	Composition %ZrO_2	%H_3PO_4	%"Zeolon H"	Drying Hr	Drying °C	Pressure Tons	Sintering Hr	Sintering °C	Modulus of Rupture psi
			Statistical Series						
1	30	23	47	40	160	15	15	500	2810 ± 70
2	30	23	47	60	150	15	15	500	2703 ± 76
3	30	23	47	40	150	15	15	500	2837 ± 46
4	30	27.15	42.85	52	144	15	15	500	2795 ± 78
5	30	23	47	40	150	15	15	500	2843 ± 150
6	30	18.85	51.15	52	156	15	15	500	2000 ± 105
7	30	30	40	40	150	15	15	500	3435 ± 23
8	30	23	47	40	150	15	15	500	2935 ± 35
9	30	23	47	40	150	15	15	500	2851 ± 34
10	30	18.85	51.15	28	144	15	15	500	3257 ± 32
11	30	27.15	42.85	28	156	15	15	500	2774 ± 219
12	30	23	47	20	150	15	15	500	3546 ± 82
13	30	18.85	51.15	28	156	15	15	500	1920 ± 37
14	30	23	47	40	150	15	15	500	2922 ± 56
15	30	27.15	42.85	28	144	15	15	500	2927 ± 13
16	30	18.85	51.15	52	144	15	15	500	2848 ± 60
17	30	27.15	42.85	52	156	15	15	500	2222 ± 50
18*	30	16	54	40	150	15	15	500	2758 ± 47
19*	30	23	47	40	140	15	15	500	3883 ± 21
20	30	23	47	40	150	15	15	500	2905 ± 70
			Additional Samples						
199-100	66.6	33.3	-	36	160	15	15	500	6025
36-054*	33.3	33.3	33.3	40	95	15	15	500	5050

*Vacuum dried at 30" mercury.

TABLE II

EFFECT OF SINTERING TEMPERATURE ON MEMBRANE STRENGTH

Membrane No.	$ZrO_2 \cdot H_3PO_4$*	H_3PO_4	"Zeolon H"	Sintering Temperature (°C)	Modulus of Rupture (psi)
191-050-1	1	1	1	250	1450 ± 89
191-050-2	1	1	1	500	2760 ± 90
191-050-3	1	1	1	750	1958 ± 118
191-050-4	1	1	1	1000	1640 ± 102

*Presintered at 500°C + 5% ZrO_2 fibers

TABLE III

RESISTIVITIES AT THREE TEMPERATURES
(Membrane No. 131-024)

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(30, 27.2, 42.8 parts by weight)

History of Membrane Material: Dried 52 hrs at 144°C
Sintered at 500°C

Relative Humidity (%)	Resistivity (ohm-cm)
Temperature 70.7°C	
84	$(3.02 \pm 0.51) \times 10^2$
37	$(6.70 \pm 0.58) \times 10^2$
13	$(8.76 \pm 0.72) \times 10^2$
0	$(5.85 \pm 0.18) \times 10^3$
Temperature 89.8°C	
85	$(1.22 \pm 0.08) \times 10^2$
46	$(4.31 \pm 0.53) \times 10^2$
30	$(6.82 \pm 0.73) \times 10^2$
10	$(9.28 \pm 0.84) \times 10^2$
0	$(7.44 \pm 0.71) \times 10^3$
Temperature 104.3°C	
61	$(1.19 \pm 0.12) \times 10^2$
51	$(2.06 \pm 0.20) \times 10^2$
26	$(4.47 \pm 0.70) \times 10^2$
11	$(7.59 \pm 1.04) \times 10^2$
0	$(4.57 \pm 1.33) \times 10^4$

TABLE IV

RESISTIVITIES AT THREE TEMPERATURES
(Membrane No. 131-023)

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(30, 23, 47 parts by weight)

History of Membrane Material: Dried 40 hrs at 150°C
Sintered at 500°C

Relative Humidity (%)	Resistivity (ohm-cm)
Temperature 70.7°C	
84	$(7.80 \pm 1.68) \times 10^2$
37	$(1.84 \pm 0.21) \times 10^3$
13	$(2.47 \pm 0.24) \times 10^3$
0	$(1.78 \pm 0.08) \times 10^4$
Temperature 89.8°C	
85	$(2.84 \pm 0.70) \times 10^2$
46	$(1.10 \pm 0.20) \times 10^3$
30	$(1.77 \pm 0.29) \times 10^3$
10	$(2.42 \pm 0.32) \times 10^3$
0	$(2.92 \pm 0.31) \times 10^4$
Temperature 104.3°C	
72	$(1.83 \pm 0.36) \times 10^2$
61	$(2.89 \pm 0.61) \times 10^2$
51	$(5.07 \pm 0.90) \times 10^2$
26	$(1.30 \pm 0.22) \times 10^3$
11	$(2.09 \pm 0.29) \times 10^3$
0	$(2.41 \pm 1.02) \times 10^5$

TABLE V

RESISTIVITIES AT THREE TEMPERATURES
(Membrane No. 131-030

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(30, 18.8, 51.2 parts by weight)

History of Membrane Material: Dried 28 hrs at 144°C
Sintered at 500°C

Relative Humidity (%)	Resistivity (ohm-cm)
Temperature 70.7°C	
84	$(2.90 \pm 1.37) \times 10^3$
37	$(7.83 \pm 3.54) \times 10^3$
13	$(1.11 \pm 0.49) \times 10^4$
0	$(1.15 \pm 0.57) \times 10^5$
Temperature 89.8°C	
85	$(9.74 \pm 3.63) \times 10^2$
46	$(4.74 \pm 2.43) \times 10^3$
30	$(8.30 \pm 4.27) \times 10^3$
10	$(1.16 \pm 0.52) \times 10^4$
0	$(2.62 \pm 2.22) \times 10^5$
Temperature 104.3°C	
72	$(4.41 \pm 0.84) \times 10^2$
61	$(9.94 \pm 1.63) \times 10^2$
51	$(2.44 \pm 0.74) \times 10^3$
26	$(7.52 \pm 2.92) \times 10^3$
11	$(1.26 \pm 0.37) \times 10^4$
0	$(4.65 \pm 3.19) \times 10^6$

TABLE VI

RESISTIVITIES AT THREE TEMPERATURES
(Membrane No. 131-026)

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(30, 18.8, 51.2 parts by weight)

History of Membrane Material: Dried 52 hrs at 156°C
Sintered at 500°C

Relative Humidity (%)	Resistivity (ohm-cm)
Temperature 70.7°C	
84	$(3.49 \pm 0.99) \times 10^3$
37	$(9.94 \pm 3.56) \times 10^3$
13	$(1.47 \pm 0.60) \times 10^4$
0	$(1.65 \pm 1.07) \times 10^5$
Temperature 89.8°C	
85	$(1.24 \pm 0.23) \times 10^3$
46	$(5.70 \pm 1.82) \times 10^3$
30	$(1.01 \pm 0.37) \times 10^4$
10	$(1.45 \pm 0.49) \times 10^4$
0	$(2.57 \pm 0.74) \times 10^5$
Temperature 104.3°C	
72	$(4.97 \pm 1.43) \times 10^2$
61	$(1.04 \pm 0.14) \times 10^3$
51	$(2.27 \pm 0.48) \times 10^3$
26	$(6.53 \pm 1.75) \times 10^3$
11	$(1.16 \pm 0.30) \times 10^4$
0	$(2.80 \pm 0.79) \times 10^6$

TABLE VII

FUEL CELL DATA

Run No.	Membrane No.	Thickness Mm	Electrode Area Cm^2	Temp °C	Ma/Cm^2 at 0.5V	Slope (RxA) Ohm-Cm^2	Resistivity at 100% R.H. Ohm-Cm	Observed Fuel Cell Resistance Ohms	Calculated Fuel Cell Resistance Ohms	Open Circuit Voltage Ohms
25	191-050 (500° sinter)	0.61	20.2	65	28.5	9.7		0.48		0.80
				89	31.7	8.1	27	0.40	0.39	0.78
				95	33.3	7.7		0.38		0.78
33	191-050 (750° sinter)	0.85	20.2	65	50.0	8.4		0.42		0.92
				90	25.5	6.4	27	0.32	0.43	0.67
35	191-050 (500° sinter)	0.83	20.2	65	35.4	10.2		0.52		0.96
				90	7.8	40.4	27	2.00	0.43	0.82
34	191-050 (750° sinter)	0.80	20.2	65	40.4	9.0		0.45		0.92
				90	Cell failed to operate					

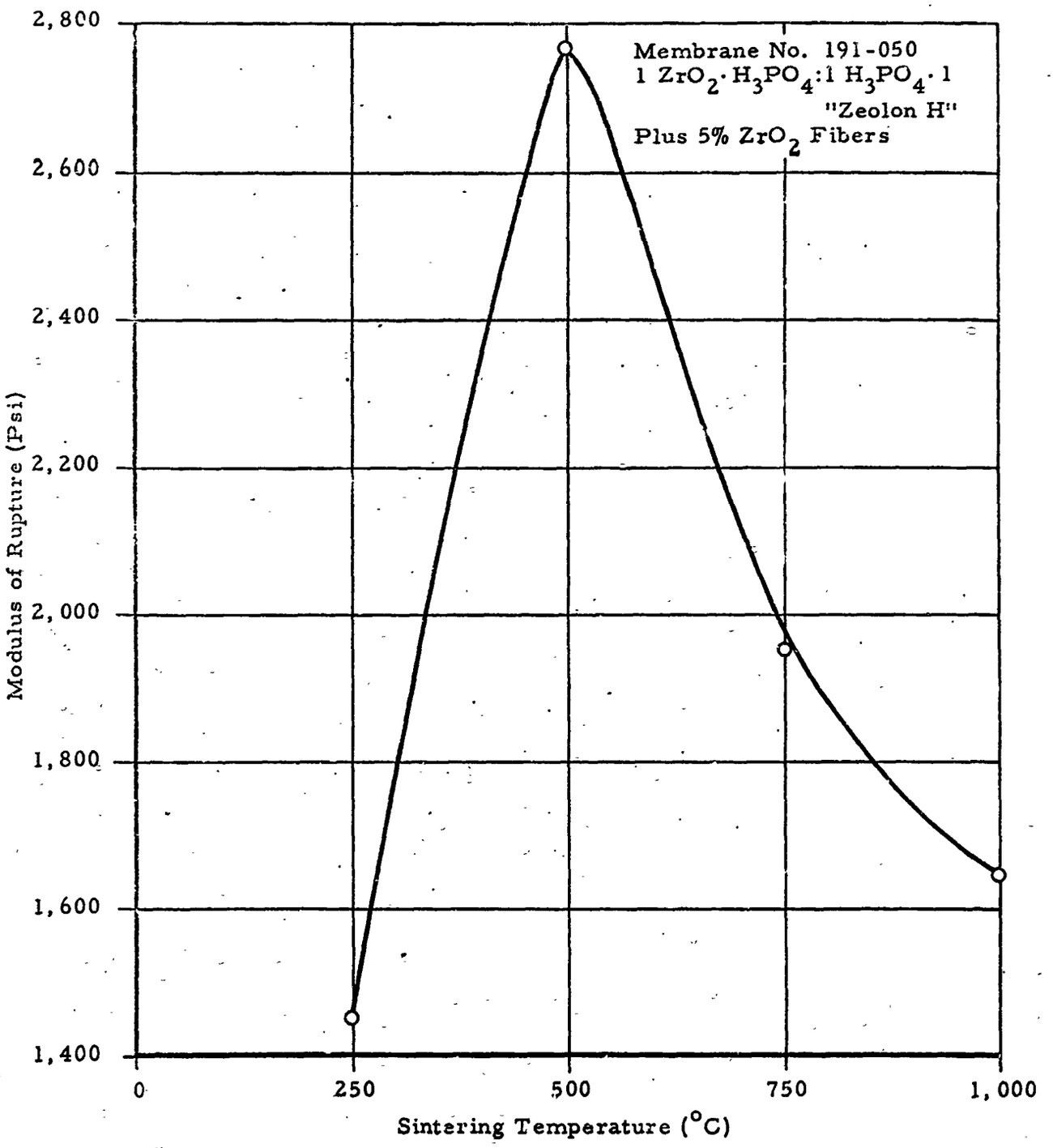

Figure 1. Effect of Sintering Temperature on Membrane Strength

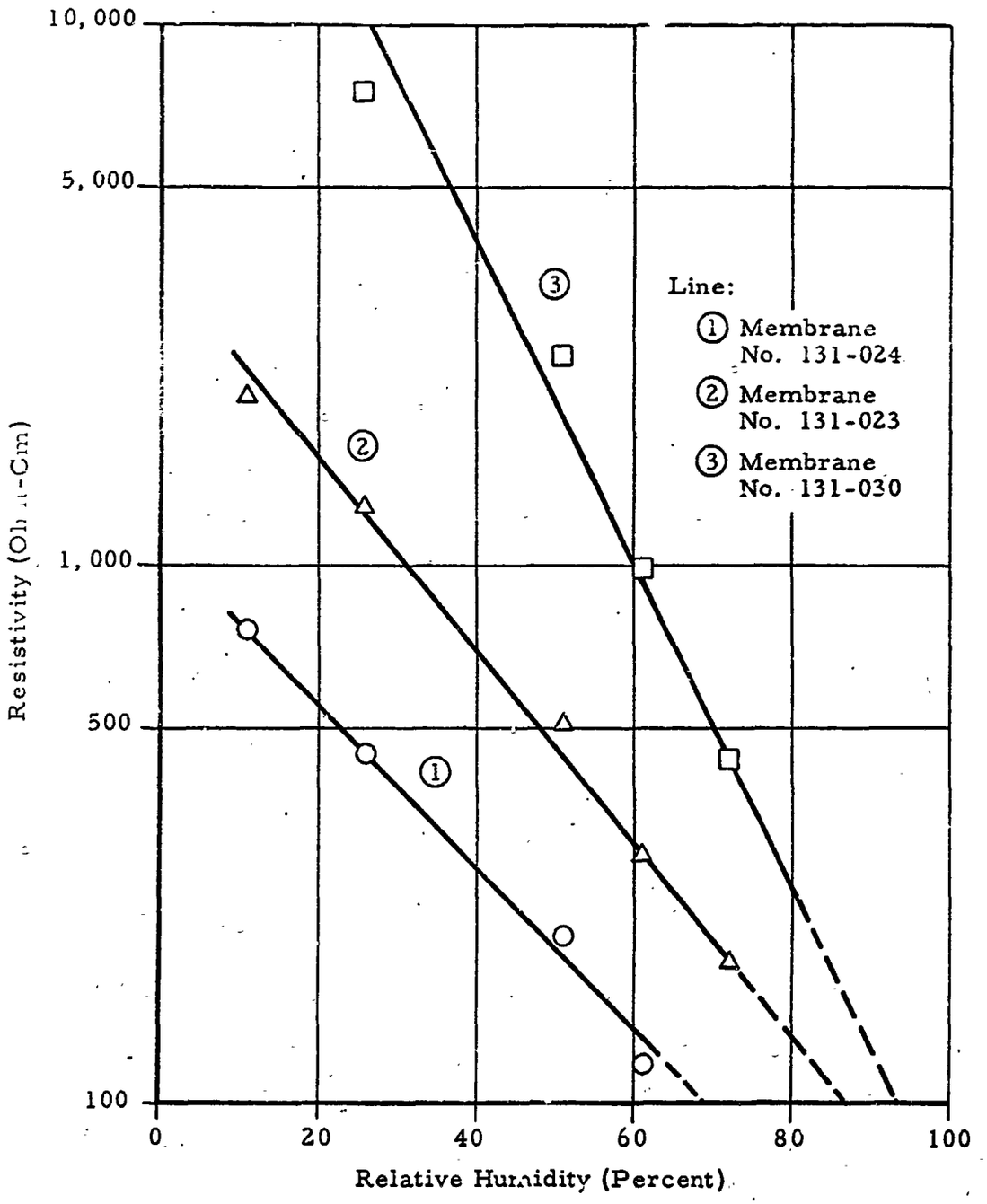

Figure 2. Comparison of Resistivities at 104°C for Three Different Membrane Compositions

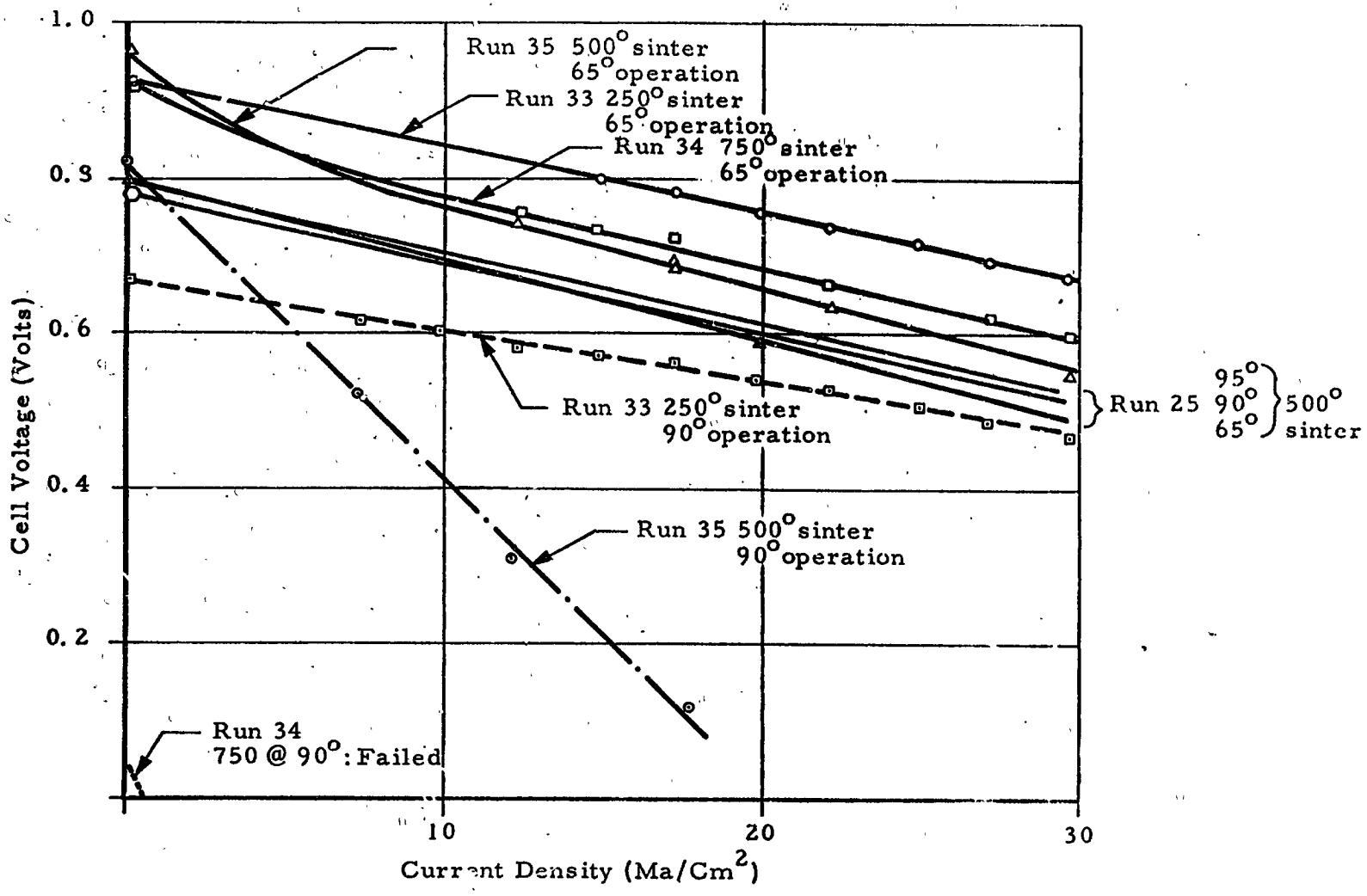

Figure 3. Polarization Curves for Membrane 191-050